SLAC-TN-07-025

Determining the Extent of Delocalization in Mixed-Valence Iron Dimers Using X-ray Absorption Spectroscopy

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August 8, 2007

Prepared in partial fulfillment of the requirement of the Office of Science, Department of Energy's Science Undergraduate Laboratory Internship under the direction of Kelly Gaffney at the Stanford Synchrotron Radiation Laboratory at the Stanford Linear Accelerator Center.

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Work supported in part by US Department of Energy contract DE-AC02-76SF00515

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ABSRACT

Determining the Extent of Delocalization in Mixed-Valence Iron Dimers Using x-ray Absorption Spectroscopy. ALISON M. HOYT (Yale University, New Haven, CT 06520) KELLY GAFFNEY (Stanford Synchrotron Radiation Laboratory, Menlo Park, CA 94025).

This study examines the extent of charge delocalization in mixed valence compounds. Understanding the structure of charge delocalization is the first step in understanding the local dynamics of charge transfer. This insight has diverse applications such as the ability to mimic biological reactions and to enhance solar technology. Because of its fast time scale, synchrotron radiation was used to probe the iron K-edge for three organometallic systems. In these complexes, two bridged metal atoms share an effective charge of 5+. In a Robin-Day Class II compound, charge is localized and the two iron atoms have effective oxidation states of 2+ and 3+ respectively. For Class III delocalized compounds each metal center has an effective charge of 2.5+. Class II/III compounds exhibit characteristics of both localized and delocalized systems according to various optical spectroscopies. Synchrotron radiation was used to study charge distribution in these poorly-understood Class II/III intermediate systems. In the limit of absolute localization, spectra of the mixed valence species were expected to be a linear combination of the reduced and oxidized species. For the delocalized case, a linear combination was not expected. These two cases were used as calibration limits to determine the extent of delocalization in the unknown Class II/III compound. Results showed that synchrotron radiation classifies the Class II/III compound as localized. However, data also demonstrated that the linear combination model did not hold as expected and a revised model is necessary to better understand this phenomenon.

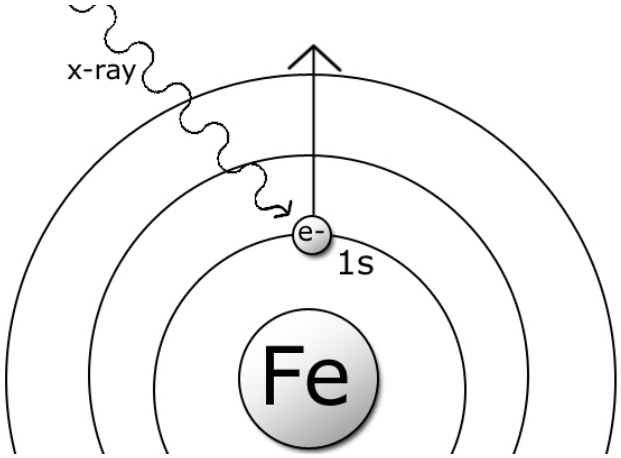
1. INTRODUCTION

X-ray absorption spectroscopy was used to study charge distribution in mixed valence organometallic complexes. These compounds consist of multiple metal atoms connected by a bridging ligand, a molecular structure that links the atoms together. A Robin-Day classification system classifies these mixed valence complexes based on the metal centers' electronic interaction [1]. Class II localized compounds consist of two metal centers with little electronic interaction. In the studied localized compound, the two iron atoms have effective oxidation states of 2+ and 3+ respectively. Class III compounds have a delocalized charge distribution with stronger electronic interaction between the two metal atoms. In this class, charge is shared between the two metal centers, which each have an effective charge of 2.5+. Many mixed valence compounds have been successfully characterized using UV/VIS and IR/NIR spectroscopy. However, an intermediate class of compounds has been discovered [2] which demonstrates characteristics of both class II and class III compounds [3]. This study examines charge distribution in poorly-understood Class II/III compounds using synchrotron based x-ray absorption spectroscopy.

Synchrotron radiation was selected because of its short time-scale. Faster than IR/NIR and UV/VIS spectroscopies because of the x-rays' shorter wavelength, x-ray absorption spectroscopy may be able to resolve processes that are time-averaged when probed with slower spectroscopic techniques. This experiment probes the transition as the Class II/III compound oscillates between a localized and delocalized state. Understanding and modeling this transition between electronic structures works toward the goal of understanding the local dynamics of charge transfer. This insight has diverse applications such as the ability to mimic biological reactions and to enhance solar technology.

Synchrotron radiation is a useful tool in the examination of x-ray absorption as its high intensity, compared with other x-ray sources, allows for more precise measurements. This radiation is produced by a synchrotron, which uses electric and magnetic fields to accelerate charged particles around a ring. The magnetic field holds the particles in their circular path, while the electric field accelerates them. Both fields are synchronized to vary with the circulating particles, producing a narrow, tightly focused beam. As the particles are accelerated, they emit photons. At SSRL, the Stanford Synchrotron Radiation Laboratory, the narrow electron beam emits broadband x-ray radiation as it passes through an undulator or wiggler. These magnetic configurations cause the electron beam trajectory to oscillate and radiate x-rays. This intense radiation is used to perform a wide variety of experiments from protein crystallography to semiconductor material analysis.

This experiment uses synchrotron radiation to perform x-ray absorption spectroscopy (XAS). Absorption peaks provide information on the electronic orbitals and local structure surrounding a specific element in the compound. X-rays are absorbed if their energy is sufficient to excite the electron to a higher energy level or completely ionize the electron. This experiment probes the iron K-edge, where 1s core electrons are excited to higher unoccupied orbitals or into the continuum.



The pre-edge absorption signal reflects electrons excited to the valence shell. This provides information on valence electron distribution and the extent of d-orbital splitting. Above the edge, the energy of the incoming x-

ray is sufficient to excite a core electron into the continuum. The outgoing electron wave scatters off surrounding atoms and interferes with the incoming x-rays, altering the measured absorption signal. Structural information on nearest-neighbor surrounding atoms is extracted from these intensity fluctuations. This experiment will combine electronic and structural information from the pre-edge and edge regions to better understand electronic distribution in class II/III compounds.

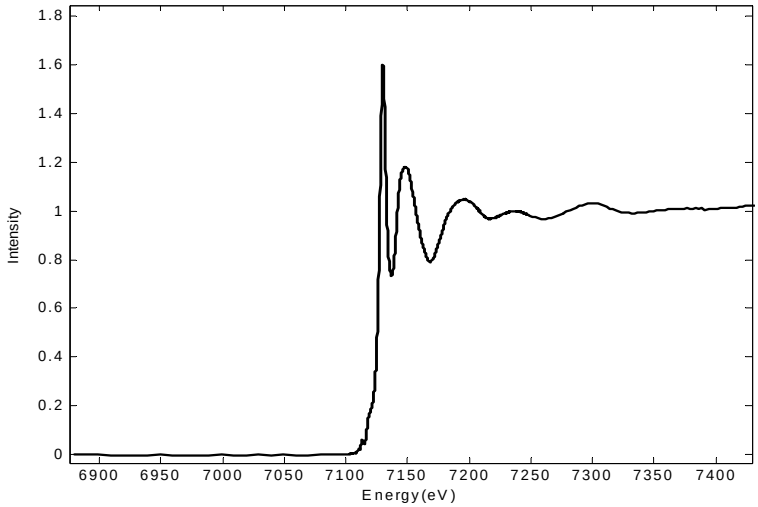


Figure. Shows the peak in absorption intensity at the edge (7125eV)

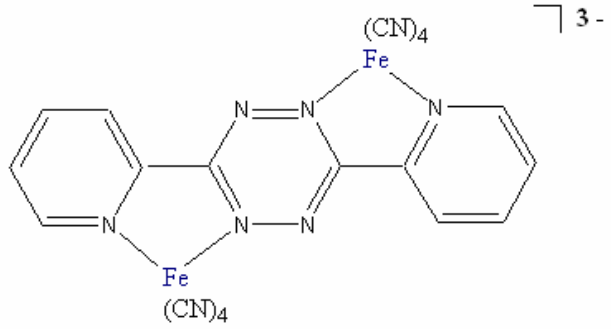
MATERIALS AND METHODS

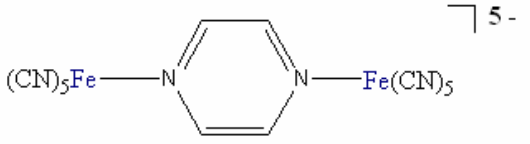
i. Theoretical Model

Class II, III and II/III compounds were each prepared in three oxidation states: both metal centers reduced, both oxidized, and a mixed valence state. XAS Spectra were taken for each of these samples to determine the extent of delocalization in the Class II/III compound. (The Class II and III compounds were used for calibration.) In a theoretical localized charge system, there is no electronic interaction between the two metal centers. Under this assumption, the absorption contribution from one metal center is completely independent of the contribution of the second iron atom. If both iron atoms in the system are reduced (2+,2+), they contribute identical spectra due to the symmetry of the molecular environment surrounding the two iron atoms. In addition, two oxidized metal centers (3+,3+) will make identical but independent contributions. In the localized mixed valence species (2+, 3+), the reduced and the oxidized iron atoms will contribute different and independent absorption spectra. The reduced iron atom will contribute an

absorption spectra identical to the completely reduced system(2+,2+). The oxidized metal center will contribute an absorption spectra identical to the completely oxidized system (3+,3+). Thus, the localized mixed valence spectra (2+,3+) will be a linear combination of the fully reduced (2+,2+) and fully oxidized (3+,3+) systems. Conversely, a linear combination of the fully oxidized and reduced spectra is not expected for the delocalized mixed valence (2.5+, 2.5+) compound. Due to electronic interaction between metal centers, the absorption spectra contributed by one iron atom is not independent of the oxidation state of the second atom. A linear combination fit was used to test this model for our Class II and III compounds. Analysis of the Class II/III fit to determine delocalization was calibrated with respect to the fully localized and delocalized compounds.

ii. Sample Preparation



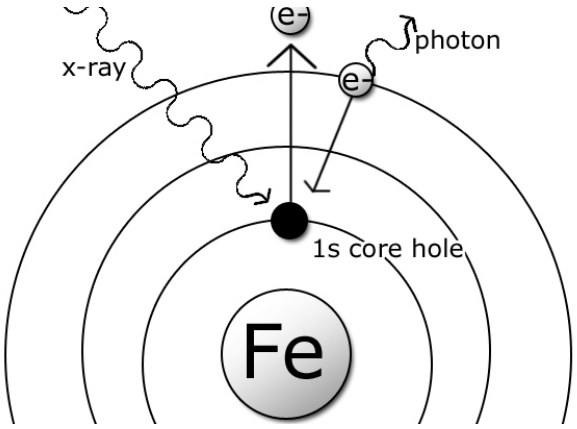


Iron based bimetallic compounds were chosen to span the Robin Day classification system. The pyrazine bridged decacyanodiiron(2+, 3+) ($(CN)_5Fe$-pz-$Fe(CN)_5^{5-}$) represented a class II system in water and a class II/III system in acetonitrile [4]. (Upper structure). The compound 3,6-bis-(2-pyridyl)-1,2,4,5-tetrazine (bptz) bridged octacyanodiiron(2+, 3+) ($(CN)_4Fe$-bptz-$Fe(CN)_4^{3-}$) in acetonitrile represented a class III system [5]. (Lower structure). The fully reduced forms (2+, 2+) of these molecules were synthesized in an inert atmosphere according to published techniques in the Keith O. Hodgson Laboratory at the Stanford University Department of Chemistry. The fully oxidized states (3+,

3+) were obtained via electrochemical oxidation of the reduced (2+, 2+) state with bromine water. The mixed-valence compounds were prepared by mixing equi-molar amounts of the (2+, 2+) and the (3+, 3+) states.

iii. XAS Data Collection and Reduction

X-ray absorption spectra were recorded at the Stanford Synchrotron Radiation Laboratory (SSRL) on beamline 7-3. The broadband radiation at this beamline is produced by a 20-pole, 2-Tesla wiggler. Radiation was monochromatized using a Si(220), Phi = 0° double-crystal monochromator over an energy range of 6900eV to 7900eV. Absorption was measured at the iron K-edge, where absorbed x-rays excite 1s core electrons to higher energy levels. The sample was placed at a 45° angle to the incident x-ray beam, in order to use a fluorescence detection setup, necessary due to the dilute nature of the samples. This setup does not directly measure reductions in transmission as incident x-rays are absorbed, but rather photons emitted from the sample, called fluorescence. This process occurs as incident x-rays excite 1s core electrons to higher energy levels. When an electron relaxes into the remaining 1s core hole, its extra energy (the difference in energy levels) is emitted as a photon. This phenomenon allows us to monitor even small changes in absorption via fluorescence. Fluorescence was measured with a 30-element Germanium detector placed at a 90° angle to the incident x-ray beam. (See Appendix Figure 1). The dilute solutions were stored in air-tight sample cells with polyethylene windows at room temperature. Energies were calibrated to 7111.2eV (the first inflection point) using an iron foil standard. In general, eight scans were measured for each



sample. EXAFSPAK was used to fit a smooth Gaussian to the pre-edge region of the averaged spectra. This fit was then subtracted from the full energy range to remove background. EXAFSPAK was also used to deglitch and spline the data. Athena used the spline to normalize all spectra intensities to 1 at 7350eV and to remove an upward sloping of the raw data at high energy.

3. RESULTS

All three compounds were compared to a linear combination of their oxidized and reduced spectra to determine the extent of delocalization. These linear combinations were not a perfect 50/50 ratio, but instead varied by compound. Optimal percentage fits were selected to minimize error between the linear combination fit and the experimental mixed valence spectra. Variation by compound was due to experimental constraints limiting precision in preparing the mixed valence species, which consisted of mixing the oxidized and reduced species. The Class II localized mixed valence experimental spectrum was fit with a 49.5% reduced (2+, 2+) and 50.5% oxidized (3+,3+) linear combination. The Class II/III mixed valence experimental spectrum was fit with a 59.0% reduced and 41.0% oxidized linear combination. The Class III spectrum was fit with a 42.3% reduced and 57.7% oxidized linear combination. The Class II mixed valence experimental spectrum was a reasonably good fit to its linear combination. There was an absolute error per point of ±0.00562nau (normalized absorption units) or ±1.4σ, where the standard deviation (σ) of the mixed valence spectra was ±0.004nau. (See Appendix Figures 2 and 3). As expected, the Class III was a poor fit to its linear combination, giving an absolute per point error twice as large at ±0.01466nau. The standard deviation also doubled to 0.009nau to maintain a comparable error of ±1.6σ. (Fig. 6&7). The Class II/III data did not fall between the Class II and Class III spectra as expected. The linear combination fit experimental data better

than anticipated. It had the lowest overall error and a comparable σ of ±0.004nau. The absolute error per point was ±0.00447nau or ±1.1σ. (Fig. 4&5).

Significant difference in error between the fit and the mixed valence spectra were seen for different energy ranges. Both the absolute error per point and the standard deviation of the mixed valence spectra were significantly lower in the pre-edge region (7109.5-7125eV) where detailed features were more finely resolved than in the edge (7125-7135eV). For example, the standard deviation value of ±0.002117 quadrupled to ±0.00840 from the pre-edge to the edge for the Class II compound. A change in scanning resolution from 0.05eV to 0.15eV at 7125eV may have contributed to this difference. The Class II compound seemed to fit relatively better in the edge (±0.857σ) than in the pre-edge (±2.17σ). The situation was reversed for the Class III compound with an error of ±2.0σ in the edge and ±1.1σ in the pre-edge region. The intermediate Class II/III compound fit well in both the edge (±0.919σ) and the pre-edge (±1.38σ). These unexpected results indicate that the intermediate compound fit the linear combination model slightly better than the Class II or III compounds.

4. DISCUSSION AND CONCLUSION

Both the absolute error and σ values vary significantly between energy regions. The error in terms of σ showed no strong trends between compounds or across energy regions. However, more valuable comparisons were made between absolute error values in similar energy regions (pre-edge vs. edge). When comparing by region and overall, the Class III compound had the largest absolute error per point, as expected. The Class II/III compound had the lowest overall error, the lowest absolute error in the pre-edge, and an absolute error comparable to that of the Class II compound in the edge. The Class III compound has a consistently larger error in its linear combination fit than the Class II compound. This data provides evidence for a localized

Class II compound and a delocalized Class III compound. These results also indicate that the Class II/III compound is marginally more localized than the Class II compound, which was expected to be the limit of localization. These trends were not revealed in the σ error values because of the uneven standard deviations between compounds. Low resolution for the more dilute Class III compound led σ error analysis to reflect an artificially good fit.

Additional error in fitting was introduced in determining the linear combination percentage. By optimizing the percentage, we unintentionally and unavoidably improved the fit for the Class III compound, even though a poor fit was expected. This error could be corrected in the future with the improved accuracy of a more precise procedure for creating the mixed valence compounds. Additional instrumental errors were considered and corrected for during data processing. This included fluctuations in the incident x-ray beam, corrected by normalizing all spectra to incident energy, and drift in the monochromator energy, corrected by calibrating the energy to an iron foil. These errors were negligible in comparison to the uncertainties generated in sample preparation.

The linear combination fit test indicated that Class III compounds are delocalized, while Class II and Class II/III compounds are localized. This localization analysis only holds if the assumed model of complete localization is applicable. This model provides a simple but insightful understanding of charge delocalization; however, analysis indicates that this simple model may not accurately explain this complex system. The linear combination model is valid in the extreme case of complete charge localization. However, even Class II compounds are rarely absolute localized systems, often maintaining some small electronic interaction between the two metal centers. Difficulties arise with such deviations from the ideal case. An ideal molecule is necessary as initial calibration to understand how spectra deviate from an absolute linear

combination with small increases in delocalization. The possibility that results may deviate from the model non-linearly makes it difficult to extrapolate from hypothetical calibration points. It is impossible to make conclusive statements about the extent of delocalization in the Class II/III compound without better understanding the Class II model calibration spectra. The differences between the Class II experimental spectra and its expected linear combination fit must be more closely probed. Further analysis of the Class II spectra may provide insight into this model of localization. However, it is clear that the Class II and Class II/III compounds fit the linear combination model significantly better than the Class III model, indicating that the x-ray absorption spectra of the Class II/III compound shares characteristics of a localized compound. This apparent localization may be due to the short time scale of the probing x-rays, which do not average over transitions on their time scale, but capture discrete states. Further experiments will allow more complete understanding of the timescales of this transition.

5. ACKNOWLEDGEMENTS

I would like to thank the Department of Energy, Office of Science and SLAC for this opportunity to participate in the SULI program. I would like to thank my mentors Kelly Gaffney, Jen Kaspar and Serena DeBeer-George as well as the rest of the Kelly Gaffney Group for their support and insight into my research.

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7. FIGURES

BL 7.3 Setup

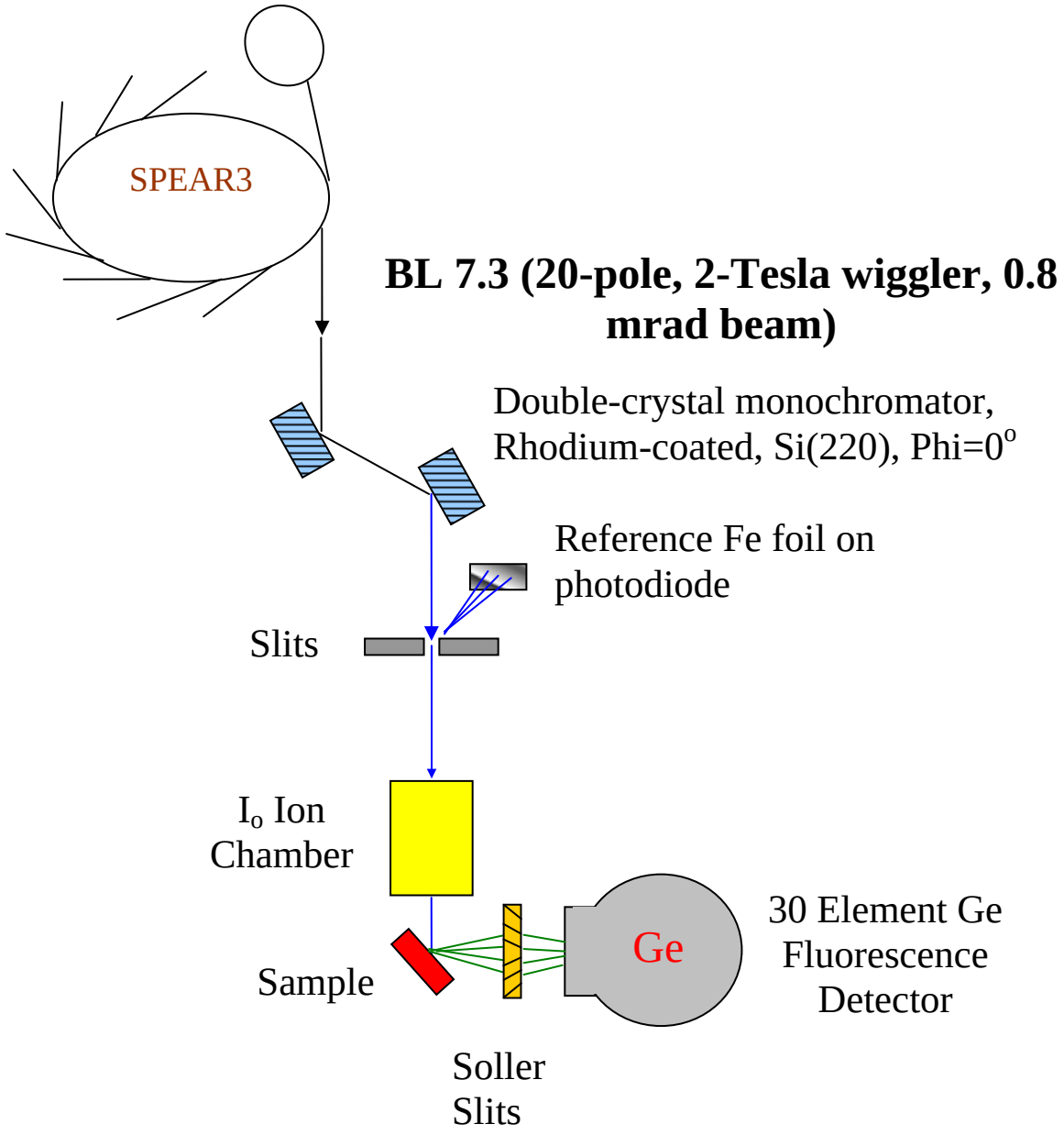

Figure 1. Diagram of the Fluorescence Detection Setup used to measure absorption.

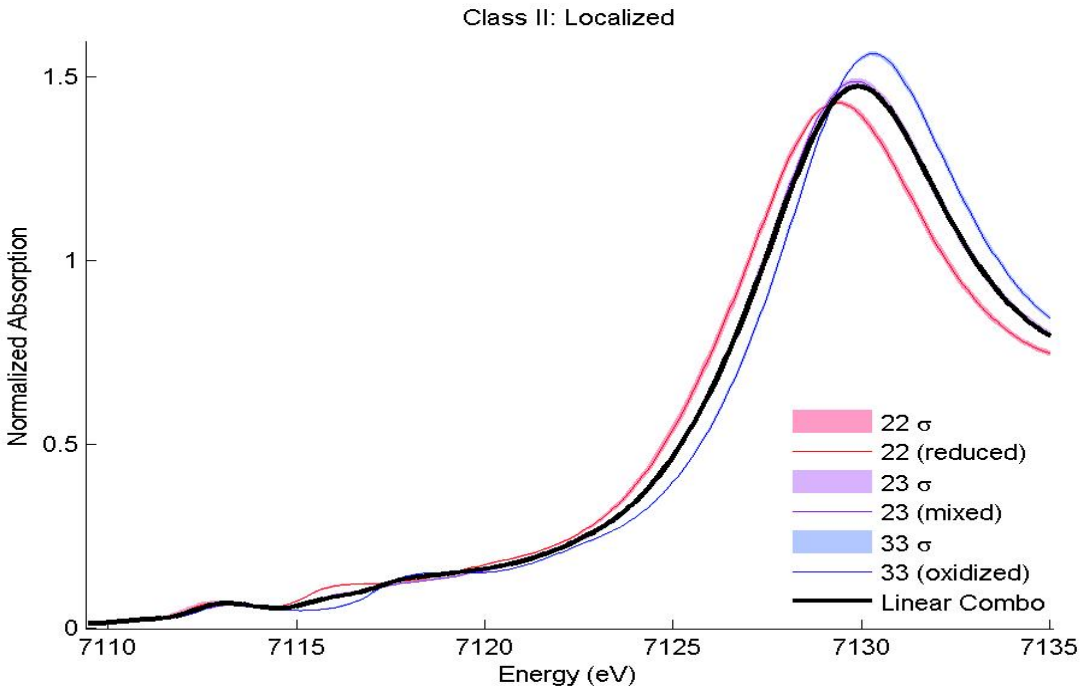

Figure 2. Absorption Spectra of the Class II localized compound. The mixed valence state (purple) was fit with a 49.5% reduced (red) and 50.5% oxidized (blue) linear combination fit.

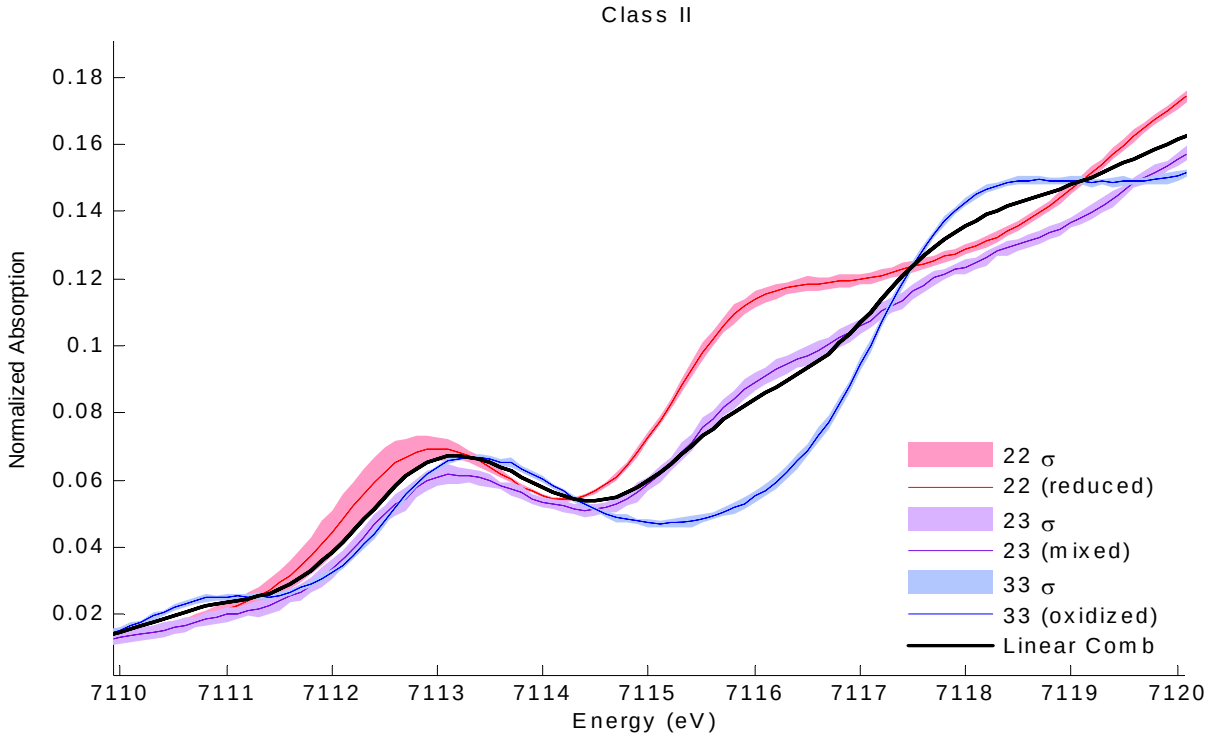

Figure 3. Absorption Spectra of the Class II localized compound zoomed in on the pre-edge energy range. The mixed valence state (purple) was fit with a 49.5% reduced (red) and 50.5% oxidized (blue) linear combination fit.

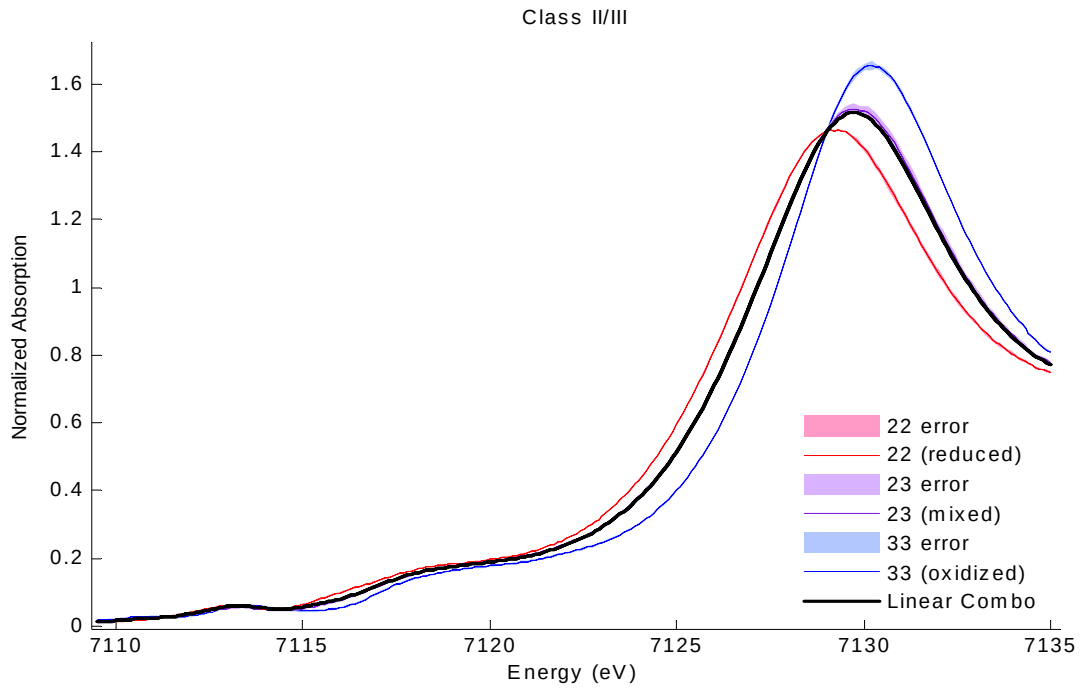

Figure 4. Absorption Spectra of the Class II/III unknown compound. The mixed valence state (purple) was fit with a 59.0% reduced (red) and 41.0% oxidized (blue) linear combination fit.

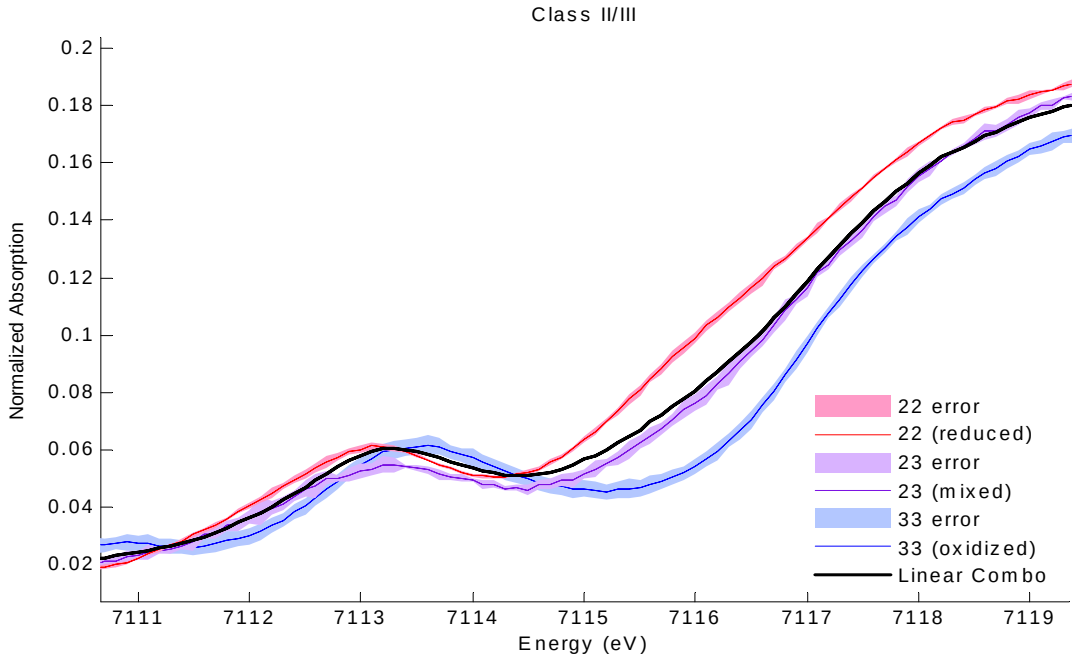

Figure 5. Absorption Spectra of the Class II/III unknown compound zoomed in on the pre-edge energy range. The mixed valence state (purple) was fit with a 59.0% reduced (red) and 41.0% oxidized (blue) linear combination fit.

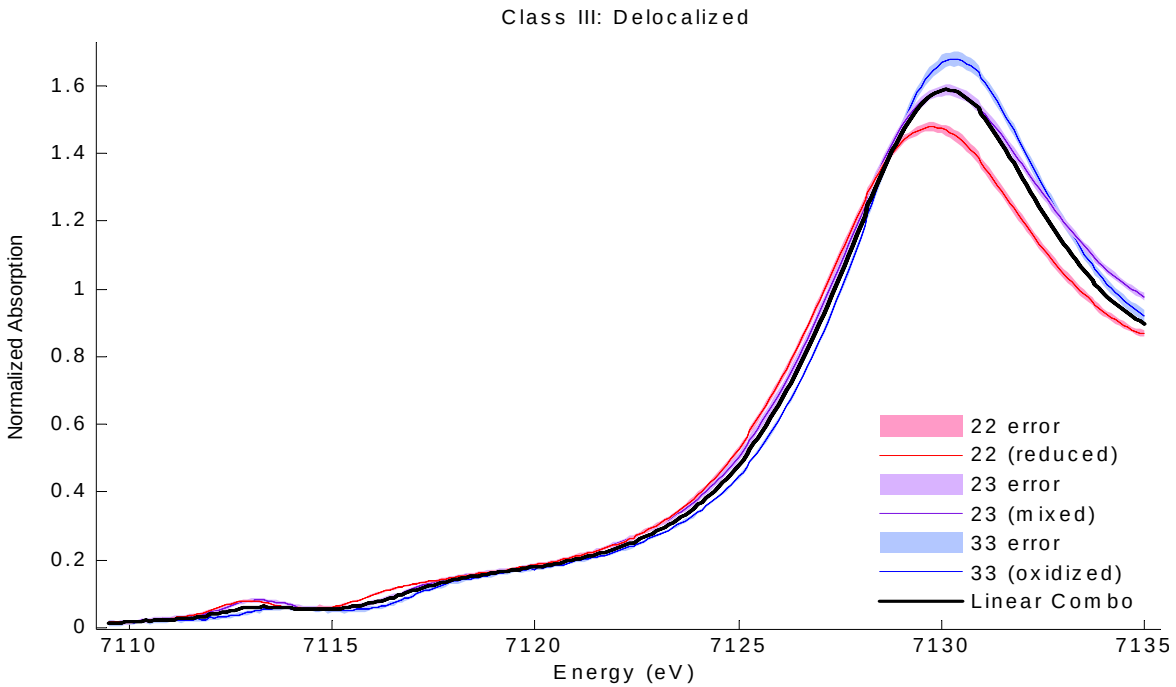

Figure 6. Absorption Spectra of the Class III delocalized compound. The mixed valence state (purple) was fit with a 42.3% reduced (red) and 57.7% oxidized (blue) linear combination fit.

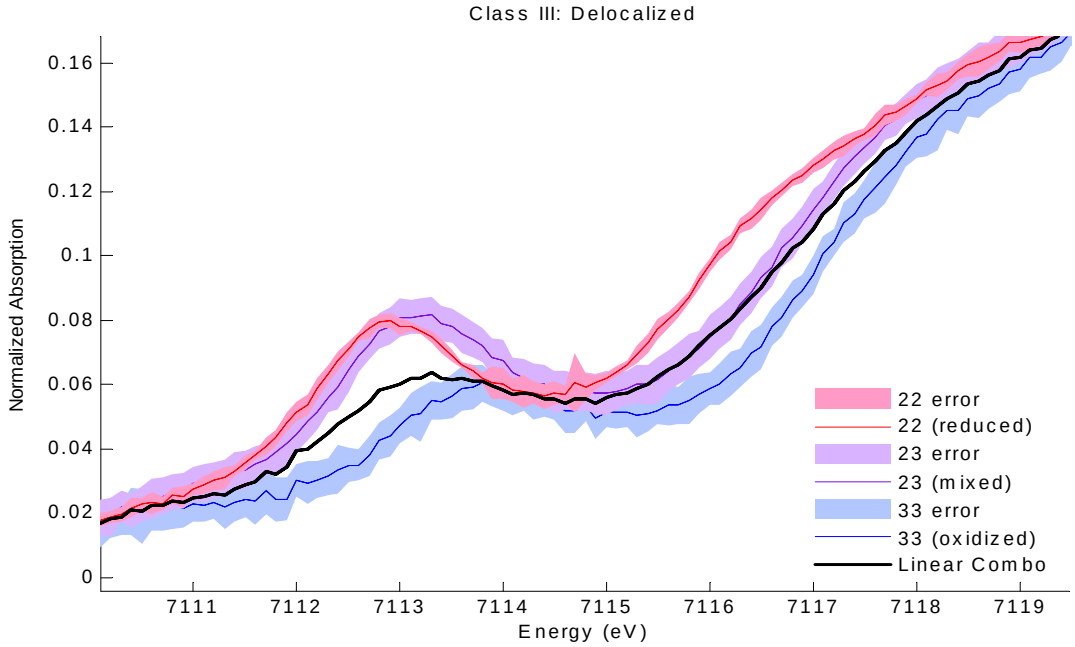

Figure 7. Absorption Spectra of the Class III delocalized compound zoomed in on the pre-edge energy range. The mixed valence state (purple) was fit with a 42.3% reduced (red) and 57.7% oxidized (blue) linear combination fit.